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Complexation of bis(8-hydroxyquinoline)-substituted tetraaza-15-crown-5 (1) (see our Technical Report No. 6) with Cu ²⁺ , Co ²⁺ , Ni ²⁺ , Zn ²⁺ , Cd ²⁺ , and Pb ²⁺ was evaluated potentiometrically in aqueous solution (0.10 M Me ₄ NCl) at 25°C. Ligand 1 formed very stable complexes with these metal ions. The UV-Vis spectra of 1 and its complexes were examined in an aqueous acetic acid buffer solution (pH 4.7). The 1-Cu ²⁺ complex provided a new absorption band at 258 nm.			
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Technical Report No. 7

**Preliminary Complexation Studies of Bis(8-hydroxyquinoline)-substituted
Tetraaza-15-crown-5 with Various Metal Ions**

by

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PRELIMINARY COMPLEXATION STUDIES OF
BIS(8-HYDROXYQUINOLINE)-SUBSTITUTED TETRAAZA-
15-CROWN-5 WITH VARIOUS METAL IONS

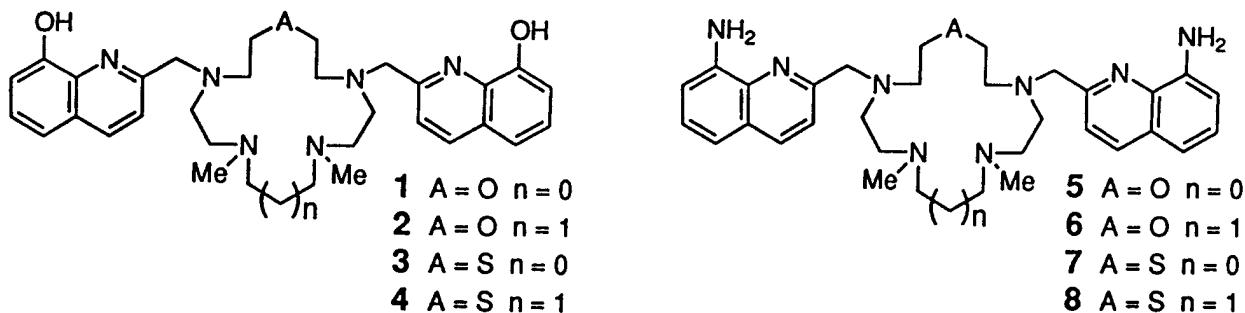
Xian X. Zhang, Jerald S. Bradshaw, R. Todd Bronson,
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Results and Discussion

A series of new 8-hydroxyquinoline- and 8-aminoquinoline-substituted tetraaza-15-

(-16)-crown-5 ethers (**1-4** and **5-8**, respectively) have been prepared in our laboratory.¹ These new ligating agents were designed to selectively bind transition and post-transition metal ions with a concomitant modulation in the absorption and fluorescent spectra of the compounds. This report gives a preliminary account of the complexation of ligand **1** with various metal ions.



Protonation and Complexation Studies of Ligand 1. Protonation constants of 8-

hydroxyquinoline-containing tetraazacrown ether **1** and stability constants for the interactions of **1** with Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} were determined by a potentiometric titration technique² at 25 °C in aqueous solution. The ionic strength was kept constant with 0.10 M tetramethylammonium chloride. The overall reactions are expressed by the general equation:



where M is the metal ion and L is the ligand. The overall equilibrium constant can be defined as

$$\beta_{pqr} = [M_p H_q L_r^{(2p+q-2r)}] / [M^{2+}]^p [H^+]^q [L^2]^r \quad (2)$$

The values of the protonation constants of the ligands and stability constants of the metal ion complexes ($\log \beta_{par}$) are listed in Tables 1 and 2, respectively.

Four protonation constants can be calculated for compound 1. The first two protonation constants ($\log K_1 = 9.55$ and $\log K_2 = 7.30$ ($16.85 - 9.55$), Table 1) and the last two constants

Table 1. Logarithms of Protonation Constants of Macroyclic Ligand **1** in Aqueous Solution (0.10 M Me₄NCl) at 25.0 °C

Reaction	$\log \beta$
$\text{H}^+ + \text{L}^{2-} \rightleftharpoons \text{HL}^-$	9.55 ± 0.05
$2\text{H}^+ + \text{L}^{2-} \rightleftharpoons \text{H}_2\text{L}$	16.85 ± 0.08
$3\text{H}^+ + \text{L}^{2-} \rightleftharpoons \text{H}_3\text{L}^+$	19.87 ± 0.09
$4\text{H}^+ + \text{L}^{2-} \rightleftharpoons \text{H}_4\text{L}^{2+}$	21.31 ± 0.14

($\log K_3 = 3.02$ and $\log K_4 = 1.44$) are close to each other. A large decrease in protonation constants is seen between the second and the third protonation steps. Since the first protonation constant of **1** ($\log K_1 = 9.55$) is hydroxyquinoline (9.65 at 25 °C, $\mu = 0.1$),³ the first two protonation constants of **1** are due to protonation of OH groups of the 8-

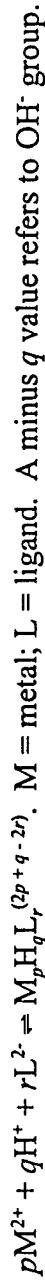
hydroxyquinoline portion and the last two forming a neutral complex with a divalent cation which may be coordinated by both the 8-hydroxyquinolines and the macroring.

Data in Table 2 show that each metal ion studied forms several types of complexes with the ligand. The 1:1 complexes ML ($p = 1, q = 0, r = 1$ in eq. 1) and M(OH)L^- ($p = 1, q = -1, r = 1$) are observed in each case. The complexes of ligand **1** with Cu²⁺, Co²⁺, Ni²⁺, Zn²⁺, Cd²⁺, and Pb²⁺ are very stable in aqueous solution. The large stability constants ($\log \beta_{\text{ML}} > 12$ and $\log \beta_{\text{MHL}} > 15$) are shown in Table 2. The most stable complexes were observed for Cu²⁺. The values of $\log \beta_{\text{CuL}}$ and $\log \beta_{\text{CuHL}}$ are 15.5 and 18.6, respectively. Cd²⁺ also forms very stable complexes with ligand **22** ($\log \beta_{\text{CdL}} = 15.3$ and $\log \beta_{\text{CdHL}} = 17.5$). Therefore, not only the fully deprotonated form of **22** (L^{2-}) but also the monoprotonated ligand (HL^-) forms very stable complexes with the metal ions studied (except for Co²⁺). In the case of Co²⁺, the complex CoHL^+ was not detected. However, Co²⁺ forms a 1:2 (M:L) complex with **1** ($\log \beta_{\text{CoL}_2} = 20.2$). A dinuclear complex with Cu²⁺, Cu₂L²⁺, was also observed. The equilibrium constants of the complexes containing hydrolysis products of the metal ions, M(OH)L^- , range from 6.44 ($\log \beta_{\text{Co(OH)L}}$) to 9.62 (\log

Table 2. Overall Stability Constants^a of Metal Ion Complexes with Macroyclic Ligand 1 in Aqueous Solution (0.10 M Me₄NCl) at 25.0 °C

<i>p</i>	<i>q</i>	<i>r</i>	$\log \beta_{pq,r}$					
			Cu ²⁺	Co ²⁺	Ni ²⁺	Zn ²⁺	Cd ²⁺	Pb ²⁺
1	0	1	15.52 ± 0.08	12.34 ± 0.04	13.46 ± 0.03	12.41 ± 0.03	15.33 ± 0.02	13.65 ± 0.03
1	1	1	18.55 ± 0.12		16.15 ± 0.18	15.55 ± 0.09	17.50 ± 0.05	16.93 ± 0.03
1	-1	1	8.53 ± 0.19	6.44 ± 0.06	7.49 ± 0.12	6.49 ± 0.05	9.62 ± 0.07	8.22 ± 0.08
2	0	1	18.92 ± 0.22					
1	0	2		20.19 ± 0.06				
1	-2	1			-3.59 ± 0.25			

^aThe equilibria of the reactions are defined by the general equation:



$\beta_{\text{Cd(OH)}_2\text{L}}$). The Ni^{2+} forms a second type of hydrolysis complex, $\text{Ni(OH)}_2\text{L}^{2-}$, which has a very low equilibrium constant (Table 2).

UV-Visible spectra. The UV spectra of free and complexed ligand 1 are shown in Figures 1 and 2. The free 1 has an absorption maximum at 244 nm. Upon addition of Cu^{2+} , a new peak develops at 258 nm (Figure 1). Other metal ions (Zn^{2+} , Pb^{2+} , Cd^{2+} , Ag^+ , Hg^{2+} , Co^{2+} , and Ni^{2+}) were also titrated with 1, but none produced a new peak or significantly interfered with the new 1- Cu^{2+} complex peak at 258 nm (Figure 2). Thus, the 258 nm peak for the 1- Cu^{2+} complex could be used for sensing purposes.

Experimental Section

Determination of Protonation and Stability Constants. The protonation and stability constants were determined by potentiometric titration in aqueous solution at 25 °C. The titrations were carried out at a constant ionic strength of 0.10 M Me_4NCl using an automatic microprocessor-controlled potentiometric titrator.⁴ Temperature was controlled within ± 0.1 °C using a jacketed cell through which water from a constant-temperature bath was circulated. Potentials to within ± 0.1 mV were measured using an Orion Model 701A Digital Ion Analyzer in conjunction with a Cole-Parmer combination electrode (Ag/AgCl reference cell). The electrode was calibrated by two precision buffer solutions, pH 4.000 \pm 0.002 and 7.000 \pm 0.002 at 25.0 °C (Cole-Parmer). Calculations were performed with the SUPERQUAD program⁵ using an IBM computer. Compound 1 was used as its adduct with HCl (1•6HCl) which had good solubility in aqueous solution (0.01 M).

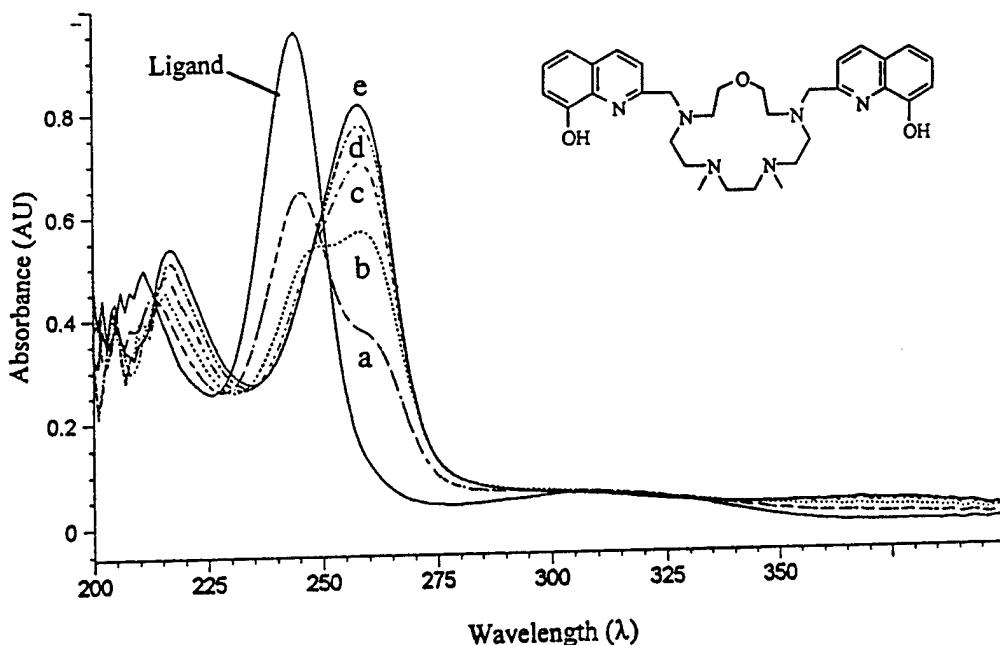


Figure 1. UV-visible spectra of free 1 and its Cu^{2+} complexes in an aqueous buffered solution. $[1] = 0.977 \times 10^{-5} M$, $[\text{buffer}] = 5.0 \times 10^{-2} M$ acetic acid ($\text{pH} = 4.7$). The labels a - e indicate 1 - 5 equivalents of Cu^{2+} added to the ligand successively.

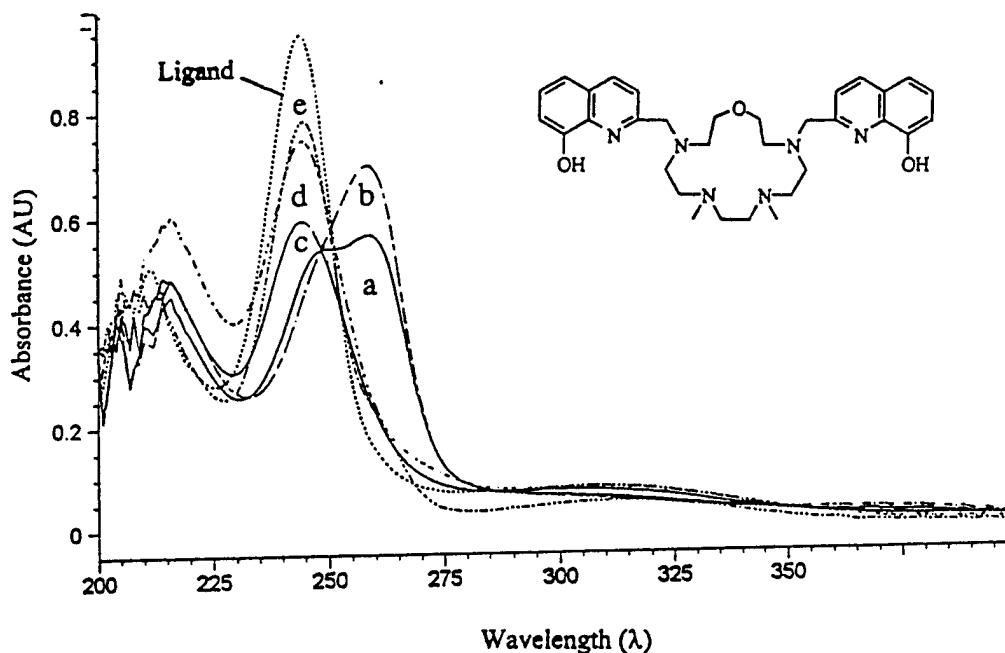


Figure 2. UV-visible spectra of free and complexed 1 in acetic acid buffer solution ($\text{pH} = 4.7$). (a and b) Cu^{2+} (1 and 2 equivalents, respectively), (c) Zn^{2+} , (d) Pb^{2+} , and (e) Cd^{2+} (2 equivalents each). $[1] = 0.977 \times 10^{-5} M$ and $[\text{buffer}] = 5.0 \times 10^{-2} M$ acetic acid.

UV-visible Spectral Measurements. UV-visible spectra were recorded at 23 ± 1 °C in a 1-cM quartz cell using a Hewlett-Packard 8452A Diode Array spectrophotometer. Both ligand and metal ions were prepared in aqueous acetic acid buffer (pH = 4.7). Concentrations of acetic and sodium acetate were 5.00×10^{-2} M and 5.00×10^{-2} M, respectively, and concentration of ligand 1 was 1.00×10^{-5} M. The metal ion concentrations were 1-5 times the ligand concentration.

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